

REVIEW OF SOME RECENT RESEARCH ON THE COMBUSTION
PROPERTIES OF COAL MACERALS

John C. Crelling
Department of Geology
Southern Illinois University
Carbondale, IL 62901 USA

K. Mark Thomas
Northern Carbon Research Laboratories
University of Newcastle upon Tyne
Newcastle upon Tyne, NE1 7RU, United Kingdom

Keywords: Macerals, Coal Combustion, Reactivity

INTRODUCTION

The work reviewed here deals with combustion studies on coal macerals, the individual plant derived substances that make up coal, and lithotypes which are associations of macerals. Studies on these components are important for two reasons. One is that broad industrial experience in pulverized fuel combustion has shown that independently of both coal rank and ash type and content, maceral composition has a significant effect on combustion. A Gondwana coal with an high inertinite content will burn differently from a similar rank Illinois Basin coal dominated by vitrinite. The particle size in pulverized fuel combustion is $70\% < 75$ micrometers. This is a size range where the particles are becoming very heterogeneous and can cover the broad range of maceral and lithotype properties. This may be a factor in carbon burn-out which is especially important in low "NOx" burners. The other reason is that the bulk of the work done on coal combustion has dealt with whole coals only and is, thus, not very informative on maceral effects.

The major difficulty in carrying out maceral and lithotype combustion work is obtaining well characterized samples. Lithotypes must be obtained in the field and usually require some further processing or cleaning up. The collection of large quantities (greater than a kilogram) is sometimes very difficult. While some vitrinite and fusinite maceral-enriched fractions can be hand-picked, the most reliable way of obtaining good concentrates of maceral groups and single macerals is by Density Gradient Centrifugation (DGC) [1-6]. For example, a typical density profile for a vitrinite-rich Herrin No. 6 coal from the Illinois Basin has a main peak in the center of the profile that represents the vitrinite group macerals while the lower and higher density tails respectively represent the liptinite and inertinite maceral groups. To get concentrates of these maceral groups, the sample is further centrifuged at two petrographically determined cut points at the maceral group boundaries. To get concentrates of single macerals, the separated maceral group samples are further subdivided in a similar manner. An easier way to get the single maceral concentrates is to separate lithotypes collected in the field. A typical example of the density profile of a fusain lithotype has two main peaks that are natural concentrations of semifusinite (lower density) and fusinite (higher density). Fractions taken from the center portion of each peak prove to be very homogeneous semifusinite and fusinite.

In using DGC techniques to obtain samples for combustion studies, three factors which need to be considered are the possible effects of the CsCl separation medium, the particle size vs. maceral liberation problem, and the representativeness of the single maceral concentrates. Although the trace amounts of the alkali metal salt (CsCl) that remain on the samples after washing might be expected to act as a catalyst during combustion, no significant effects have been found in combustion experiments [7]. In experiments dealing with pulverized boiler fuel, the particle size is still too coarse to liberate most of the liptinite and some inertinite macerals, and the product will, therefore, contain a large number of mixed phase particles. In the case of the inertinite macerals, this problem can be greatly reduced by using fusain lithotype samples as the feed. In regard to the question of how well the maceral samples represent a pulverized fuel that may have a significant proportion of mixed phase particles, it was found in a series of coal combustion profile experiments [7] that the individual maceral group profiles could be proportionally combined to match the combustion profile of the whole coal sample.

COAL COMBUSTION PROFILE EXPERIMENTS

Maceral group concentrates from a rank series of Oklahoma coals were used in a set of experiments in which the samples were combusted in air in a TGA at a heating rate of 15°C per minute [7]. Compared to the whole coals, the maceral concentrates showed similar rank trends e.g., the temperatures of combustion onset, maximum combustion rate, 50% burn-off, and char burn-out all increased with rank, but were more reproducible, more linear, and less variable. Of the maceral groups the vitrinite began combustion at a slightly higher temperature than the other macerals, but it burned significantly faster and more intensely. Semifusinite temperatures, excluding combustion onset, were generally higher and the maximum rate of weight loss was lower than that of the coexisting vitrinite. The few sporinite samples that were studied were initially more reactive than the other macerals, but they became less so at higher temperatures. They had the highest char burn-out temperatures and the lowest maximum rate of weight loss. It should also be noted that the variation in combustion properties due to maceral effects are of the same order of magnitude as the rank effect. This observation confirms earlier work [8].

COAL AND CHAR EXPERIMENTS

In another recent set of experiments the combustion properties of a channel sample of the Herrin No. 6 coal, its selected lithotypes, single maceral concentrates, and associated chars were studied [9-10]. The chars were made in an Entrained Flow Reactor at 1000°C in a nitrogen atmosphere at heating rates comparable to pulverized fuel conditions (10^4 to 10^5 °C second⁻¹). The chars were then combusted in a TGA in an atmosphere of 80% argon and 20% oxygen and the combustion gases were analyzed in a mass spectrometer.

The results of ultimate analyses show that compared to the whole coal channel sample the DGC vitrinite had slightly less carbon and about half the sulfur content, while the DGC fusinite had slightly more carbon and about two-thirds less hydrogen and nitrogen. In the corresponding chars, the nitrogen increased by almost one-third in the vitrinite and by about two-thirds in the fusinite.

The morphology of the chars were strikingly different. The extremes were the uniform open thin-walled cenospheres of the DGC vitrinite and the totally unfused and unchanged forms of the fusinite. The semifusinite showed a mix of thick-walled open cenospheres, thick-walled honeycombed cenospheres, and unfused particles. The char from the whole coal showed a proportional mix of all these forms.

The differences in reactivity (rate of weight loss) in temperature programmed experiments are also striking. While the DGC vitrinite is just slightly more reactive than the whole coal which has about 85% vitrinite, the DGC fusinite was only about half as reactive. The DGC semifusinite is intermediate between these two extremes. Thus, there can be a wide variation in reactivity between different coal particles from the same sample.

The gas evolution profiles of these samples also show some strong similarities and differences. The temperature programmed TGA runs of the chars all show a dominant CO₂ peak with a lower intensity CO peak of the same shape and position (see Figure 1. a,b,c). The SO₂ release is bimodal with a peak before the start of CO₂ evolution related to inorganic sulfur and one just after the CO₂ maximum related to organic sulfur. The peak of nitrogen evolution consistently occurs well after the main CO₂ peak although there is a lower temperature shoulder suggesting two release mechanisms or two types of nitrogen functionality. Work on model compounds of nitrogen suggests that the pyrrolic and pyridinic functionality may be responsible [11-12]. The results on the combustion of the coal samples were generally similar except for a low temperature shoulder in all the curves representing volatile release (Figure 2. a,b,c).

The biggest differences between the vitrinite and fusinite DGC maceral profiles were that both the vitrinite coal and char were more reactive than the fusinite. For example, the temperature of 50% and 100% burnout for the vitrinite coal samples were 443°C and 549°C respectively, while for the fusinite they were 558°C and 705°C. For the chars the same temperatures for the DGC vitrinite were 489°C and 565°C respectively, while for the fusinite they were

557°C and 720°C. However, a higher proportion of the inherent nitrogen in the fusinite was converted to NO. For example, in the coal combustion the ratio of NO/N for the DGC vitrinite was 0.19 while for the fusinite it was 0.29. The same figures for the char combustion were 0.08 for the vitrinite and 0.19 for the fusinite.

This variation in conversion of fuel nitrogen to nitric oxide can be explained by differences in reactivity leading to varying degrees of NO reduction on the carbon. A higher percentage of the nitrogen content in the fusinite maceral is converted to nitric oxide. Thus, while the nitrogen contents of the macerals decrease in the order: vitrinite > semifusinite > fusinite, the conversion of the coal and char nitrogen to NO shows the reverse order. Therefore, there appears to be a compensation effect whereby the amount of NO evolved from the macerals is similar.

REFERENCES CITED

1. Dyrkacz, G.R. and Horowitz, P.E. Fuel 1982, 60, 3
2. Dyrkacz, G.R., Bloomquist, C.A.A., Ruscic, L., and Horowitz, E.P. Fuel 1984, 1166
3. Dyrkacz, G.R., Bloomquist, C.A.A., Ruscic, L. and Horowitz, E.P. 1984, in Chemistry and Characterization of Coal Macerals, eds. R.R. Winans and J.C. Crelling, American Chemical Society Symposium Series 252. Washington D.C., 67-77
4. Dyrkacz, G.R., Bloomquist, C.A.A. and Soloman, P.R. Fuel 1984, 63, 536
5. Karas, J., Pugmire, R.J., Woolfenden, W., Grant, D.M. and Blair, S. International Journal of Coal Geology 1985, 5 315
6. Crelling, John C., Ironmaking Proceedings-AIME, 1988, 43, 351
7. Crelling, John C., Hippo, Edwin J., Woerner, Bruce A., and West Jr., David P., Fuel, 1992, 71, 151
8. Crelling, J.C., Skorupska, N.M. and Marsh, H. Fuel 1988, 67, 781
9. Crelling, John C., Thomas, K. Mark, and Marsh, Harry, Fuel, 1993, 72, 339
10. Hindmarsh, Christopher J., Wang, Wanxing, Thomas, K. Mark, and Crelling, John C., Fuel, (in press)
11. Wang, W. and Thomas, K. M., Fuel, 1992, 71, 871
12. Spracklin, C. J., Stanczyk, K., Thomas, K.M., Marsh, H., Edwards, I. A. S., and Skorupska, N.M., Proceedings of the 1990 International Carbon Conference, 1990, p.330

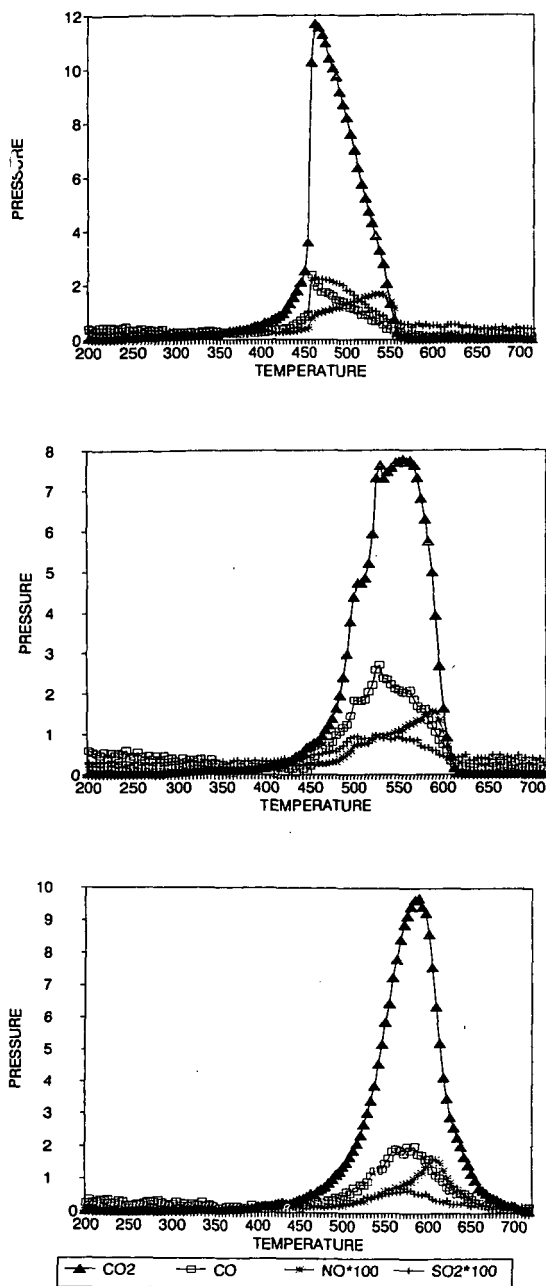


FIGURE 1. Gas evolution profiles of maceral chars combusted in an atmosphere of 80% Argon and 20% Oxygen, 1a (top) vitrinite, 1b (middle) semifusinite, 1c (bottom) fusinite. Note the shift in the peaks from top to bottom indicating decreasing reactivity.

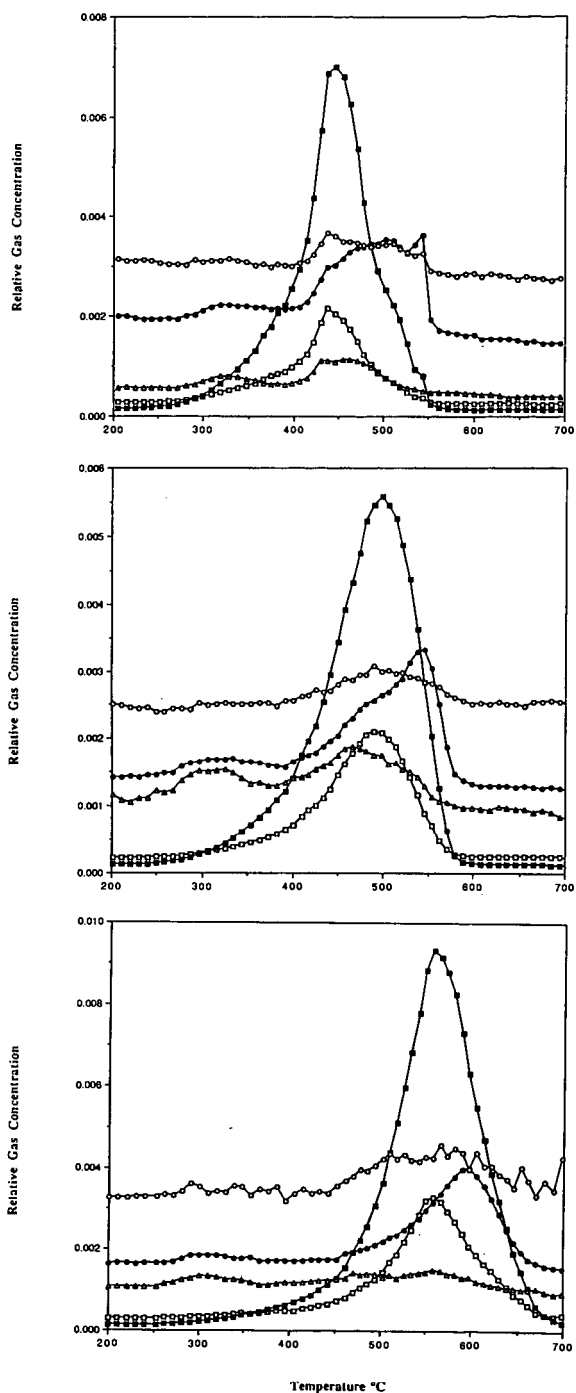


FIGURE 2. Gas evolution profiles of coal macerals combusted in an atmosphere of 80% Argon and 20% Oxygen, 1a (top) vitrinite, 1b (middle) semifusinite, 1c (bottom) fusinite. Note the shift in the peaks from top to bottom indicating decreasing reactivity. KEY: (\square) CO, (\blacksquare) CO_2 , (\bullet) $\text{NO} \times 100$, (Δ) $\text{HCN} \times 100$, (\circ) $\text{N}_2 \times 70$.